

# The Kinetics and Mechanism of the 'Multi-site' Phase Transfer Catalyzed Dichlorocarbene Addition to Norbornylene and 2, 5-Norbornadiene

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## ABSTRACT

Three step synthesis of a water - soluble multi - site phase transfer catalys (MPTC-I), viz.,  $\alpha$ ,  $\alpha^1$ ,  $\alpha^{11}$  -tris(triethyl ammonium methylene bromide)  $\beta$ -hydroxy ethyl benzene is described. The potentiality of MPTC-I is demonstrated by studying the kinetic aspects of the reactions, viz. dichlorocarbene addition to norbornylene and 2, 5-norbornadiene.

**Keywords:** dichlorocarbene addition-stirring speed-concentration of NaOH- catalyst amount - kinetics of dichlorocyclopropanation.

## 1.1 INTRODUCTION

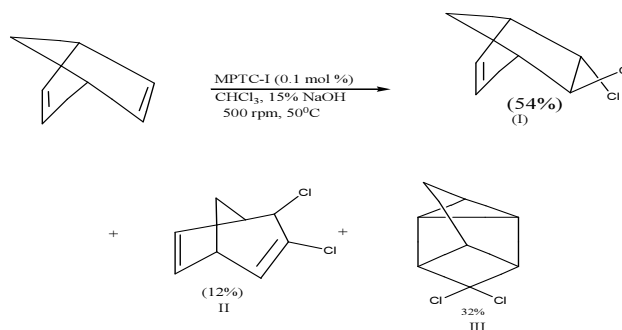
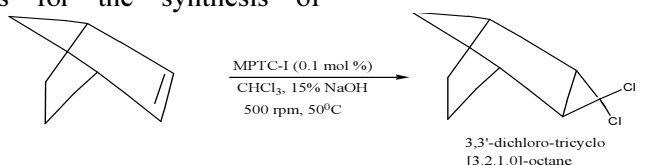
Dichlorocarbenes are considered to be synthetically useful species for the preparation of gemdihalocyclopropanes. The addition of dihalocarbenes to olefins, a reaction discovered by Doering and Tarber<sup>1</sup> has provided an exceptionally useful synthesis of the norcarane ring formation. When acyclic olefins are employed, the dihalides are relatively stable but certain cyclic olefins have been found to be undergoing rearrangement to give ring

expanded products. Preliminary study of the addition of carbenes to systems capable of undergoing rearrangement, it has been examined a model which was expected to reflect the classical stereo specific addition of dihalocarbenes to olefins. The addition of halocarbenes to norbornylene<sup>2</sup> gave a product ( $C_8H_{10}Cl_2$ ) isomeric with the expected dichlorocyclopropane derivative. This isomer was shown to be 3,4-dichloro bicyclo [3.2.1] octane-2. Jefford et.al.,<sup>3</sup> reported first the homo 1,4- addition of dichlorocarbene to norbornadiene. Treatment of 2, 5-norborna-

diene with dichlorocarbene did not give such clear-cut results as compared to norbornylene. The reaction of 2,5-norbornadiene with dichlorocarbene gave the same mixture of three 1:1 adducts in total yields of 50% and 3-10% respectively. Reactions involving dihalocarbenes that were believed to require strict anhydrous conditions and strongly basic agents can be performed in the presence of aqueous sodium hydroxide and quaternary ammonium catalyst. Makosza *et al.*,<sup>4</sup> had successfully demonstrated the generation of dichlorocarbenes and its addition with norbornylene, which gave rise to the formation of norcaranes. The use of crown ether and quaternary ammonium salts to catalyze dichlorocarbene addition with a wide variety of substrates has been documented. Moore *et al.*,<sup>5</sup> reported the utility of octopus compounds as useful phase transfer catalysts for the synthesis of

norcaranes from the reaction of dichlorocarbene to norbornylene and 2,5-norbornadiene in the excess of aqueous sodium hydroxide and chloroform. Bergman<sup>6</sup> reported that the dichlorocarbene addition to norbornylene in an aqueous/organic bi-phase system in the presence of benzyl triethyl ammonium chloride gave 3,4-dichloro bicyclo [3.2.1] octane. Addition of dichlorocarbene to norbornadiene<sup>7,8</sup> gave a dihalide fraction with a molecular composition of  $C_8H_8Cl_2$ . The NMR spectrum of the product clearly established that it consisted of a mixture of predominantly three compounds in the relative amount 54:12:32.

The dichlorocarbene addition of norbornylene and 2,5-norbornadiene was investigated with emphasis on kinetic aspect using the newly synthesized MPTC-I. (Scheme-1 and 2).



- (I) = 3, 3<sup>1</sup>-dichloro –tricyclo[3.2.1.0<sup>2,4</sup>] oct-6-ene  
 (II) = 3, 4-dichloro –bicyclo [3.2.1] oct-2,6-diene  
 (III) = 1, 4 –dichloro-tetracyclo[3.3.3.0.0.0]-octane

**Table 1- Effect of MPTC-1 on the rates of dichlorocarbene addition to reactions norbornylene and 2,5 –norbornadiene**

Type of Variation	variable parameters	Rates of the reaction ( $k_{\text{obs}} \times 10^4, \text{S}^{-1}$ )	
		norbornylene	2,5-norbornadiene
<b>Stirring Speed (rpm)</b>	100	0.43	2.22
	200	0.54	3.17
	300	0.73	3.74
	400	1.68	4.80
	500	1.84	4.81
	600	1.85	4.81
	700	1.85	4.83
	800	1.87	4.85
<b>Catalyst Amount (mmols)</b>	0.10	0.36	2.98
	0.15	0.63	4.21
	0.20	1.22	4.91
	0.25	1.46	5.90
	0.30	2.59	7.23
<b>Substrate Amount (mmols)</b>	5.31	2.54	7.47
	10.62	1.89	3.53
	15.93	1.56	3.42
	21.24	1.24	2.60
	26.55	0.88	1.40
	31.86	0.65	1.30
<b>[NaOH] (M)</b>	3.41	0.53	2.73
	4.41	0.87	4.42
	5.49	1.21	4.93
	6.65	1.59	5.37
	7.89	1.88	6.61
<b>Temperature (K)</b>	313	0.44	3.57
	318	0.72	4.31
	323	0.89	4.88
	228	1.35	6.56
	333	1.67	7.24

## 1.2. RESULTS AND DISCUSSION

The dichlorocarbene addition of norbornylene and 2, 5-norbornadiene was investigated with emphasis on kinetic aspects using the newly synthesized MPTC-I

(Schemes-1 and 2). The kinetic experiments for the dichlorocarbene addition to norbornylene and 2, 5-norbornadiene were conducted under bi-phase conditions with excess of 15% w/w aqueous NaOH and chloroform under pseudo-first order

conditions. The reaction was studied at a stirring speed of 500 rpm in the temperature range 25-45°C. The catalyst was conditioned with aqueous NaOH and chloroform for 10 minutes before the substrate was added to the reaction mixture and the samples were collected from the organic layer at regular intervals of time. The kinetics of dichlorocarbene additions to norbornylene / 2,5 -norbornadiene was following the disappearance of norbornylene/ 2,5-norbornadiene using gas chromatographic technique. The effect of stirring speed, amount of catalyst, substrate concentration, sodium hydroxide concentration and temperature on the reaction rate constants is efficiently executed using PTC technology (Table.1) Based on the experimental results obtained, a suitable mechanism is proposed for both the systems.

### 1.2.1. Effect of stirring speed

The effect of varying the stirring speed on the rate of dichlorocarbene addition to norbornylene and 2, 5-norbornadiene with chloroform and aqueous NaOH were studied in the range 100-800 rpm. From the plots of  $\log(a-x)$  versus time, pseudo-first order rate constants were evaluated. A plot of  $k_{obs}$  against stirring speed is shown in Fig.1. The kinetics of the reaction is independent of the mass-transfer limited domain; the rate constants of the reaction as stirring increase and levels off to a constant value above the stirring speed (500rpm). At 500 rpm, anion exchange equilibrium is relative to the organic displacement reaction and the substrate consumption rate becomes independent of the rate of stirring. Similar observation was reported independently by many workers<sup>9,10</sup> reflect kinetic control by

mass transfer of the chemical reaction ( $Q^+ X^-$ ) is at a steady state concentration. In a systematic kinetic study of dichlorocarbene addition under solid/liquid phase transfer catalysis in the presence of t-BuOK, Klumpp *et.al.*,<sup>11</sup> reported the dependence of stirring speed on the reaction rate constants above 200 rpm and infers the operation of interfacial mechanism. Below 500 rpm, diffusion controlled kinetics is observed. Hence the independence of the reaction rate constants on the stirring speed above 600 rpm in the present study is indicative of extraction mechanism. Similar trend of stirring speed was observed in our earlier studies *viz.*, dichlorocarbene addition to styrene<sup>12</sup> and C-alkylation<sup>13</sup> of phenyl acetone using ethyl iodide.

Dichlorocarbene addition to norbornadiene and 2, 5- norbornadiene under PTC conditions.

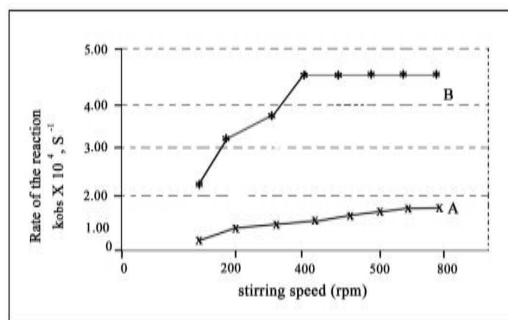
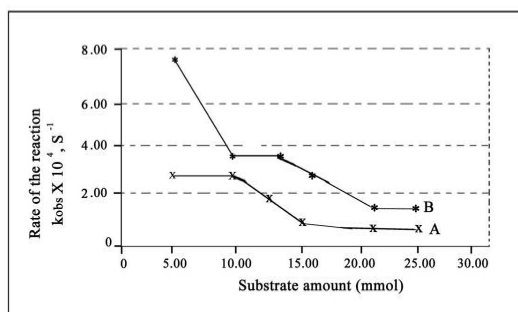


Fig.1 Effect of stirring speed variation for the dichlorocarbene addition to (A) norbornylene and 2, 5-norbornadiene

### 1.2.2. Effect of substrate amount

Varying the amount of norbornylene and 2, 5-norbornadiene from 5.3-31.9 mmol and keeping other reagents such as chloroform and 15% w/w NaOH in excess performed kinetic experiments. Pseudo-first

order rate constants are evaluated from the linear plots of  $\log(a-x)$  versus time (Fig.2.) The observed decrease in the reaction rate constants may be attributed to the proportionate decrease in the number of the catalytic active sites available. The results suggest that the concentration of the substrate in the organic phase is not important and the concentration of the substrate at the interface may be vital.

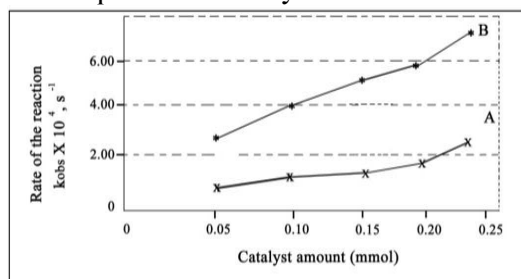


**Fig.2** Effect of variation of substrate amount for the dichlorocarbene addition to (A) norbornylene (B) 2, 5-norbornadiene

### 1.2.3. Effect of catalyst amount

The amount of catalyst was varied from 0.1-0.3 mol% (based on the substrate amount) and the experiments were conducted using 15% w/w aqueous NaOH solution. The rate constants are plotted against the weight of the added catalyst (mmol). The rate constants are linearly dependent on the amount of the catalyst used in each reaction. The increased rate constants are attributed to the increase in the number of active sites. In the absence of the catalyst, no product was detected even after 4 hours of the reaction. Only a catalytic amount (0.1 mol% based on the substrate) is required in order to obtain good yields of the product. The linear dependence of the reaction rate constants on the catalyst concentration shows that the

reaction is believed to proceed through extraction mechanism. Similar dependence of pseudo – first order rate constants for the dechlorocarbene addition reaction of cis 1, 4-polybutadiene<sup>14</sup> was reported earlier. On the contrary, Carman et.al.,<sup>15</sup> observed a linear increase in the rate constant with the amount of catalyst up to 13.2 mol% where the rate levels off in the study of dichlorocarbene addition to bicyclo [3.2.1] oct -2-ene under solid/liquid PTC in the presence of 50% NaOH. Further it was also reported that the phenomenon can be attributed to the limited interfacial area in the system, which becomes saturated with catalyst molecules, and so further addition has only a minor effect on the observed rate. In the present study, a bilogarithmic plot of the reaction rate constants versus the concentrations of the catalyst gave a straight line having a slope 0.4 for norbornylene and 2.4 for 2, 5-norbornadiene (Fig.3). In the study of dehydrobromination of phenyl ethyl bromide in the presence of tetra acetyl ammonium bromide, zero order kinetics with respect to the catalyst was observed<sup>16</sup>.

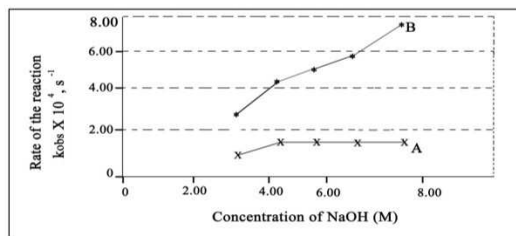


**Fig.3** Effect of catalyst amount for the dichlorocarbene addition to (A) norbornylene (B) 2, 5-norbornadiene

### 1.2.4. Effect of sodium hydroxide Concentration

The rate of dichlorocarbene addition to norbornylene and 2,5-norbornadiene

strongly depends on the strength of the NaOH. Kinetic experiments were carried out employing 3.41-7.89 M aqueous NaOH. Pseudo-first order rate constants are evaluated from the plots of  $\log(a-x)$  versus time. The reaction rate constants are strongly influenced by the concentrations of aqueous NaOH. The observed rate constants tremendously increased with increase in basicity of hydroxide ion. In the study of dichlorocarbene addition to norbornylene / 2,5-norbornadiene in a phase transfer catalytic system, Walter *et al.*,<sup>17</sup> observed that the extraction of norcaradiene (using PTC) is more effective, if the base concentration in the aqueous alkaline solution is higher. In a kinetic study of the dichlorocarbene addition to hexane-1 by PTC, KOH is used as a base rather than sodium hydroxide, as KOH enhances the reaction rate. In this case, the reaction rate initially increases and then decreases gradually when the concentration of KOH increases due to the catalytic decomposition at higher KOH concentration. In our present study, the rate constant increases with increase of base concentration. A bilogarithmic plot of the reaction rate against sodium hydroxide concentration, gives a straight line having a slope of 0.7 for dichlorocarbene addition to norbornylene and 1.0 for 2, 5-norbornadiene (Fig.4). In our study of dichlorocarbene addition to norbornylene and 2, 5-norbornadiene using chloroform and MPTC-I, the kinetic order with respect to aqueous NaOH concentration was found to be 0.7 and 1.0. In the case of dichlorocarbene addition to cis -1, 4 -polybutadiene<sup>18</sup>, the effective kinetic order with respect to aqueous NaOH was found to be 2.3, where extraction mechanism is operative.



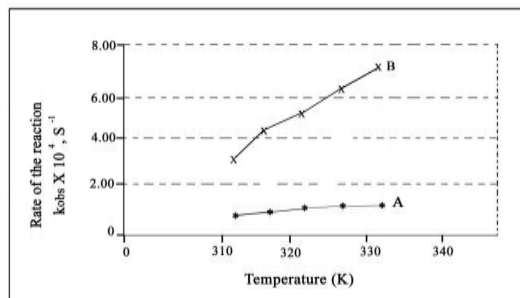
**Fig.4 Effect of variation of concentration of NaOH for the dichlorocarbene addition to (A) norbornylene (B) 2, 5-norbornadiene**

### 1.2.5. Influence of temperature variation

The effect of varying temperature on the rate of dichlorocarbene addition to norbornylene / 2,5-norbornadiene was studied in the temperature range 25- 45°C. The kinetic profile of the reaction is obtained by plotting  $\log(a-X)$  versus time. The rate constants increase with increase in temperature. The energy of activation is calculated from Arrhenius plot  $E_a=9.2 \text{ K cal mol}^{-1}$  for norbornylene and 7.3 for 2, 5-norbornadiene. The other thermodynamic parameters,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  for norbornylene and 2, 5-norbornadiene are evaluated and presented in Table.2. The activation energy for the ethylation of pyrrolidin – 2- one under PTC condition was reported to be  $12.4 \text{ K cal mol}^{-1}$  and for this an interfacial mechanism was proposed. In a comprehensive study of the dichlorocarbene addition to isobutylene, it has been observed that the formation of 1,1-dichloro-2, 2-dimethyl cyclopropane increases with increases of temperature and the  $E_a$  value was found to be  $12.32 \text{ K cal mol}^{-1}$ . Osipova *et al.*,<sup>19</sup> observed a favorable effect on the extraction of tetra butyl ammonium hypochlorite ion-pair from the aqueous phase into the organic phase on increasing the temperature in the study of the oxidation

of benzyl alcohol by hypochlorite ion under PTC conditions. The dehydrobromination of phenyl ethyl bromide proceeded more rapidly in the presence of tetraoctyl ammonium bromide. But the zero order kinetics in the presence of catalyst and low energy of activation ( $8 \text{ K cal mol}^{-1}$ ) suggested a hydroxide ion extraction mechanism governed by diffusion control. The  $E_a$  of intra-particle diffusion of anion exchange resins in aqueous solutions is of the order of  $6\text{-}9 \text{ K cal mol}^{-1}$ . Shih *et. al.*,<sup>20</sup> studied the effect of temperature on the rate for the formation of phenyl benzoate in the presence of  $\text{TBAHSO}_4$  as PTC and without PTC. The activation energies calculated from the corresponding Arrhenius plots are  $7.89 \text{ K cal mol}^{-1}$  with  $\text{TBAHSO}_4$  and  $3.72 \text{ K cal mol}^{-1}$  respectively, without PTC. In this case an extraction mechanism has been proposed.

The observed energy of activation for the dichlorocarbene addition to norbornylene and 2,5-norbornadiene are  $9.2 \text{ K cal mol}^{-1}$  and hence hydroxide ion extraction mechanism is proposed for the reaction under study, which is governed by diffusion control (Fig.5).



**Fig.5** Effect of variation of temperature for the dichlorocarbene addition to (A) Norbornylene (B) 2, 5-Norbornadiene

**Table.2** Thermodynamic parameters.

Substrate	$E_a$ $\text{Kcalmol}^{-1}$	$\Delta H^\ddagger$ $\text{Kcalmol}^{-1}$	$\Delta S^\ddagger$ $\text{CalK}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger$ $\text{Kcalmol}^{-1}$
norbornylene	9.2	5.49	-178.5	56.14
2,5 -norbornadiene	7.3	6.70	-174.3	54.80

### 1.3. Comparison of reaction rate constants

A comparison of reaction rate constants of the two dichlorocarbene additions can be attempted since all the reactions were conducted at identical reaction conditions taking 20ml chloroform, 0.1 mol% catalyst (MPTC-I) and 25% W/W NaOH. The reactions were run at  $45^\circ\text{C}$  with a stirring speed of 500rpm. The observed rate constants ( $k_{obs}/10^{-4}, \text{s}^{-1}$ ) for norbornylene and 2,5-norbornadiene are found to be

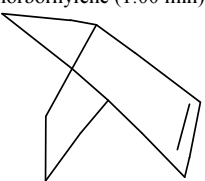
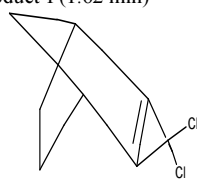
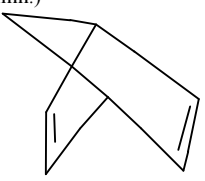
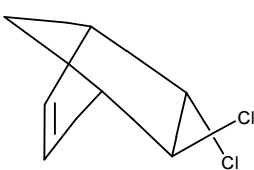
2.55 and 5.44 respectively. These values are in approximate ratio 2:1 (2, 5 – norbornadiene: norbornylene). The reaction rate of 2, 5-Norbornadiene is twice faster than norbornylene and this can be attributed to comparatively electron rich nature of 2, 5-Norbornadiene, which readily attaches to the electron deficient dichlorocarbene. The transition state of 2, 5 – norbornadiene is far less hindered than norbornylene which makes 2, 5-norbornadiene more reactive than norbornylene which makes 2, 5-norbornadiene more reactive than

norbornylene. The reaction rates and the amount of catalysts used are listed below:

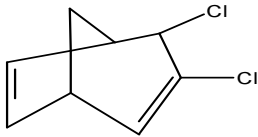
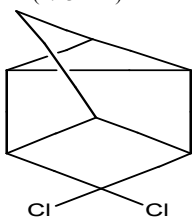
**Table: 3.comparison of reaction rate constants with different catalysts.**

Entry	Catalyst	Amount (mol %)	$k_{obs} / 10^{-4}, S^{-1}$	
			norbornylene	2,5-norbornadiene
A	None	None	Nil*	Nil*
B	MPTC-I	0.1	2.55	5.44
C	MPTC-II	0.1	1.85	4.80
D	SPTC	0.1	0.73	2.22

\*No Conversion after 3 hours catalysts.

S. no	Substrate with experimental conditions	Products (S)	% Conv <sup>a</sup> with Reaction time	Spectral data <sup>b</sup>	Ref.
1	norbornylene (1.00 min)  1. Subs. amount: 2.0 g 2. Cat. amount: 7.04mg (0.1mol %) 3. Solvent: CHCl <sub>3</sub> ; 20 ml 4. [NaOH] : 15%w/w, 25ml(4.41m) 5. Temp: 50°C	Product-I (1.62 min) 	99.00; One hour	<sup>1</sup> H-NMR: T=7.3-9.2(m) <sup>13</sup> C-NMR: δ=68.08(C3), 34.53,32.48,30.75,24.17 (C-1,C-6,C-2, C-4); 33.02;31.54,30.32 (C-5, C-7, C-8)	16
2	2,5-norbornadiene (1.06 min.)  1. Subs. amount: 2.0 ml 2. Cat. amount: 7.04mg, (0.1 mol%) 3. Solvent: CHCl <sub>3</sub> ; 20 ml 4. [NaOH]: 15%w/w, 25ml (4.41M) 5. Temp. 50°C	Product-I (1.69 min.) 	98.00; (54+12+32) One hour	Product-I IR (neat) $\nu_{Cm}^1$ : 3040, 1625, 725, <sup>1</sup> H-NMR(CDCl <sub>3</sub> / TMS): δ=6.7-6.5 (dd,2H) 5.97-5.86 (t,4H), 4.89-4.44 (dd,2H) 3.65-2.9 (m,2H)	17



S. no	Substrate with experimental conditions	Products (S)	% Conv <sup>a</sup> with Reaction time	Spectral data <sup>b</sup>	Ref.
3		Product-II 1.91 min  Product-III (2.43 min) 		Product-II IR (neat) $\nu_{\text{Cm}}^1$ 3040, 1608, 738, 690. <sup>1</sup> H-NMR (CDCl <sub>3</sub> /TMS): $\delta$ = 6.17(dd,2H), 6.10 (t,1H) 5.64 (m, 6H) 2.9-1.5 (m,6H)  Product-III <sup>1</sup> H-NMR (CDCl <sub>3</sub> /TMS): $\delta$ = 2.98-2.85(m,2H) 2.74-2.61 (m,1H) 2.19-1.99 (m,1H) 1.751.60(m,4H), HRMS (m/z), C <sub>8</sub> H <sub>8</sub> Cl <sub>2</sub> : Calculated: C: 36, H: 3.05. Found: C:36.42, H:3.21	

The above results reflect a comparative trend among the different catalysts used. Based on the observed rate constants, it is evident that the MPTC-I in 60% and 75% more active than the MPTC-II and “single-site”TEBAB respectively. The much lower rate constants obtained on using “SPTC” were attributed to the diffusional – limitations of the rates under bi-phase conditions.

#### 1.4. Multi-site phase transfer catalyst –I'S activity in hydroxide –ion initiated reactions.

The results shown in Table-3 establish the synthetic utility of the new MPTC-I under PTC/OH<sup>-</sup> conditions. Control experiments of dichlorocarbene addition to olefin in the absence of the catalyst resulted in <1% conversion in three hours. As is evident from Table 3 the new MPTC-1 is perform extremely well for hydroxide-ion

initiated reaction systems resulting in excellent yield of the products. All the dichlorocarbene addition reaction were conducted at identical reaction conditions taking 20 ml chloroform, 0.1 mol% catalyst (MPTC-I) and 15% W/W NaOH. The reactions were run at 50<sup>0</sup>C with a stirring speed of 500 rpm. The reactions were run at 50<sup>0</sup>C with a stirring speed of 500 rpm. The reaction viz., dichlorocarbene addition to olefins such as norbornylene and 2,5-norbornadiene yield 99.00% and 98.00% conversion with in one hour. **A**:% conversion by gas chromatography, **B**: for known compounds only selected spectral data given.

#### 1.4. Mechanism

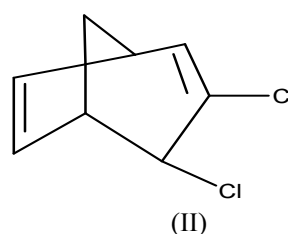
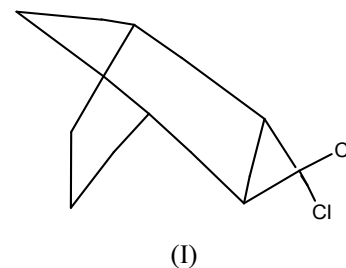
The dichlorocarbene addition to norbornylene and 2, 5-norbornadiene provides evidence for two important steps viz., the formation of the electron deficient:

$\text{CCl}_2$  followed by the addition of the dichlorocarbene.

In the phase transfer system, two major mechanisms believed to be operative are the Starks's extraction mechanism<sup>21</sup> (characterized by reaction rate with increased organophilicity, independence of reaction rate on stirring speed above certain value and liner dependence of reaction rate on catalyst concentration ) and Makosza's interfacial mechanism<sup>22</sup> (characterized by maximum reactivity with relatively hydrophilic quats, usually alkyl triethyl ammonium quats, increased reaction rate with increased speed even up to 1950 rpm and fractional; order with respect to catalyst).

The addition of dichlorocarbene to norbornylene and 2,5-norbornadiene by phase transfer method, are found to undergo rearrangement to ring expanded products gave an adduct for norbornylene in an isolated yield of 99.0% and three 1:1 adducts for 2,5-Norbornadiene in an overall yield of 98.0% (54.0%+12.0%+32.0%). They were separated by gas-liquid chromatography and identified by NMR spectroscopy. From the observed experimental results, it is clear that the dependency of the kinetic data on the stirring speed up to 500 rpm, concentration of the catalyst, aqueous hydroxide ions, temperature and higher  $E_a$  value are consistent with the hydroxide ion extraction mechanism. Giamician and Dennstedt<sup>23</sup> reported that the reaction of the potassium salt of pyrrole with chloroform gave 3-chloro-pyridine. Parham and Reiff<sup>24</sup> studied the dichlorocarbene addition to indene; the product is rearranged at 500 in ethanol in a first order reaction to give  $\beta$  - chloronaphthalene and hydrogen chloride.

Skell *et al.*,<sup>25</sup> reported that silver ion rearrangement of 6,6-dihalobicyclo [3.1.0] hexane gave the 2-bromo-2-cyclohexen-1-ol ring system. The addition of dichlorocarbene to norbornylene yielded 3,3- dichloro-exo-tricyclo [3.2.1.0] octane (I), which was, rearranged with great facility to exo-3,4-dichlorobicyclo [3.2.1] oct-2- ene (II). The NMR allowed configurationally assignments and was presented in detail (Table.4). The rearrangement of I and II exhibited pseudo – first order kinetics at 450C carried out in  $\text{CHCl}_3$ ; the rate being strongly affected by the dielectric constant of the solvent was considered to be indicative of an iron – pair intermediate being formed in the rate – determining step with rapid conversion to II.

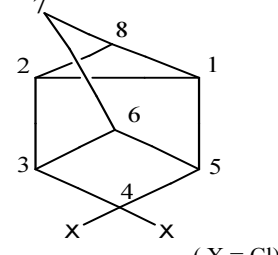


In the case of 2, 5 – norbornadiene, an examination of the total product by Gas – liquid chromatography indicated the presence of not less than three products. These substances distilled in a narrow range [72-90<sup>0</sup>C (4.3-4.7mm.)], indicating that they are probably isomeric. The component

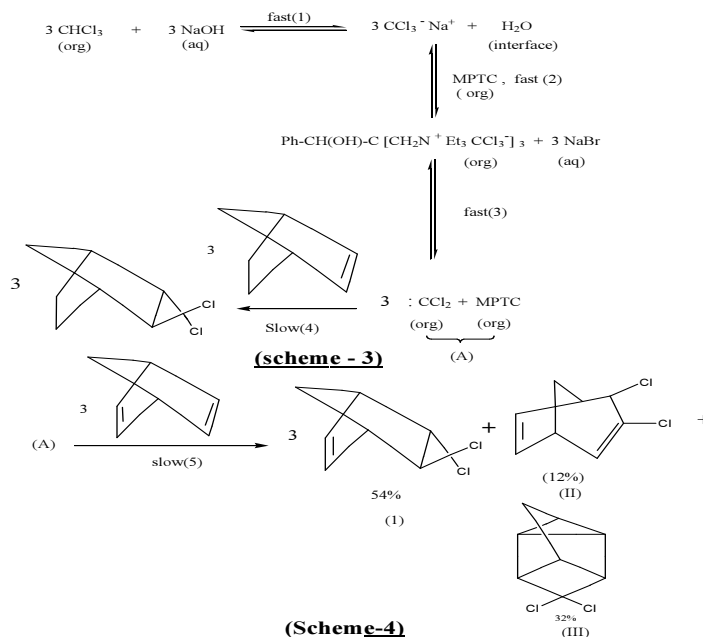
present in the largest amount was concentrated by low- temperature distillation to about 94% purity, but refinement to a greater degree was not possible in our hands. This substance was 3, 3 – dichloro – exo-tricyclo [3.2.1.0] oct -6- ene, as indicated by its NMR spectrum and its facile conversion on standing to exo – dichlorobicyclo [3.2.1] octa -2, 6-diene. The exo configurations were inferred by comparisons of the NMR spectra with those of the corresponding product from norbornylene. In addition to the usual rearrangement products deriving from exo and endo, 2- addition, the homo 1, 4 adduct was isolated in appreciable quantity. It was easily characterized by comparison of its  $^1\text{H}$  and  $^{13}\text{C}$  resonance spectra with those of the dichloro analogue. In this case the tetracyclic skeleton is unambiguously identified by the six distinct  $^{13}\text{C}$  signals. The reports in the literature which state that various carbenes apparently

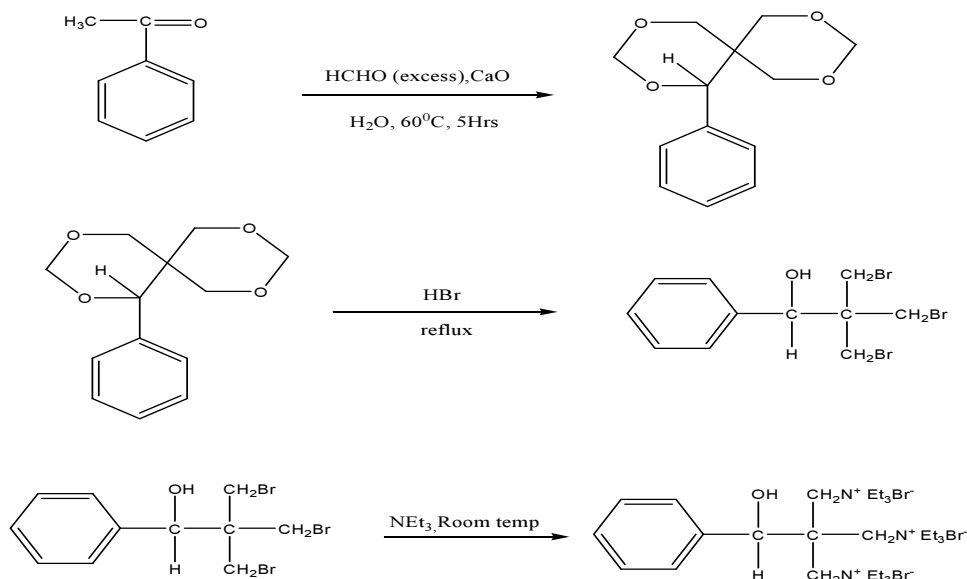
only give 1, 2 – adducts with 2,5-norbornadiene.

**Table.5.**  $^{13}\text{C}$ -resonance spectra of dichlorotetracyclo [3.3.3.0.0.0] octane. Values expressed in ppm downfield from  $\text{Me}_4\text{Si}$  in  $\text{CDCl}_3$  as solvent.

1,4-adduct of 2,5-norbornadiene	$^{13}\text{C}$ -Signals	X=Cl
 (X = Cl)	$\text{C}_1, \text{C}_2$	18.26
	$\text{C}_8$	31.02
	$\text{C}_7$	34.27
	$\text{C}_6$	41.42
	$\text{C}_3, \text{C}_5$	57.76
	$\text{C}_4$	92.04

The mechanism of the dichlorocarbene addition to norbornylene and 2,5-norbornadiene using chloroform under PTC conditions may be written as follows:





### 1.5. Experimental General

$^1\text{H}$  NMR (400MHz) and  $^{13}\text{C}$  NMR (100MHz) spectra were recorded on a JEOL-GSX-400 NBFT-NMR spectrometer with  $\text{Me}_4\text{Si}$  as internal standard. Mass spectra and HRMS were obtained on a Finnegan mat 8230 mass spectrometer. Elemental analysis was carried out on a Heracus-CHN-Rapid Analyzer and IR spectra were measured on a Perkin-Elmer model 983 IR spectrometer.

#### 1.5.1 Synthesis of 1-phenyl-2, 4,8,10 – tetraoxaspiro (5.5) undecane

One litre three necked-flask was fitted with a mercury seal with an efficient stirrer and placed in a thermostat. Acetophenone  $37\text{cm}^3$  (30.9g), formaldehyde (37-41% solution.) in excess and water

( $150\text{cm}^3$ ) were placed in a flask and the mixture was stirred well. Calcium oxide (15g) dissolved well in water ( $50\text{cm}^3$ ) was added in small portions. The reaction was carried out at  $60^\circ\text{C}$  for five hours. To the cold reaction mixture 50% ice cold  $\text{H}_2\text{SO}_4$  was added until the filtered sample gave no precipitate. A few drops of oxalic acid added till a filtered sample gave evidence of the absence of calcium. It was reduced to one-third volume by steam distillation. The viscous liquid was extracted with chloroform and dried over anhydrous  $\text{MgSO}_4$ . The compound was distilled and collected at  $1.5\text{mm}/167^\circ\text{C}$  by vacuum distillation. Yield: 62.5%, m.p. $86^\circ\text{C}$ , FTIR (KBr);  $\lambda_{\text{max}}$ : 3010, 2880, 1580, 1170, 763  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR(400MHZ,  $\text{CDCl}_3$ ): $\delta$ :135.9, 128.2, 127.0,94.5,82.7,71.0,69.6,66.3,36.8,(found:236.10287, $\text{C}_{13}\text{H}_{16}\text{O}$  requires 236.10486).

### 1.5.2. Synthesis of tris (methylene bromide) $\beta$ – hydroxyethyl benzene

1-phenyl-2, 4, 8, 10-tetra oxaspiro (5.5) undecane (6g, 0.254mol) was taken in a 500ml single necked round bottomed flask, 80 cm<sup>3</sup>hydrobromic acid (47% solution) was added to it. It was refluxed gently for 8 hours. The contents were extracted with chloroform. The pure compound was separated using column chromatography on silica gel. A low melting solid deep yellow in color was obtained in 48% yield (found: 400.732, C<sub>11</sub>H<sub>13</sub>OBr<sub>3</sub>requires 400.834).

### 1.5.3. Synthesis of $\alpha$ , $\alpha^I$ , $\alpha^{II}$ -tris (triethyl ammonium methylene bromide) $\beta$ –hydroxyethyl benzene (MPTC-I)

This (methylene bromide)–hydroxyl ethyl benzene (2.5g) was dissolved in dry benzene (25cm<sup>3</sup>) was added over a period of 2hours. Dry nitrogen was bubbled through the reaction mixture for 24 hours. The mixture was stirred using a magnetic stirrer for 100 hours. Then the precipitated “multi-site” quaternary ammonium salt was extracted with water in which it was completely soluble (scheme.5.). It was found to be highly hygroscopic. Yield 98%, FTIR (KBr)  $\lambda_{\text{max}}$ :3400,2880,2678,2440,1457,767 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz,D<sub>2</sub>O): $\delta$ :7.8-7.4 (5H,m,ArH), 4.8-3.15(24H,m,-CH<sub>2</sub>), 4.55 (1H,s,->C-H),2.25(1H,s,-OH),1.45-1.05 (27H,m,-CH<sub>3</sub>).Analysis for C<sub>29</sub>H<sub>58</sub>ON<sub>3</sub>Br<sub>3</sub> (Calculated C:49.44%; H:8.3%; N:5.96%; found C:48.98%; H:8.3%; N:5.50%)

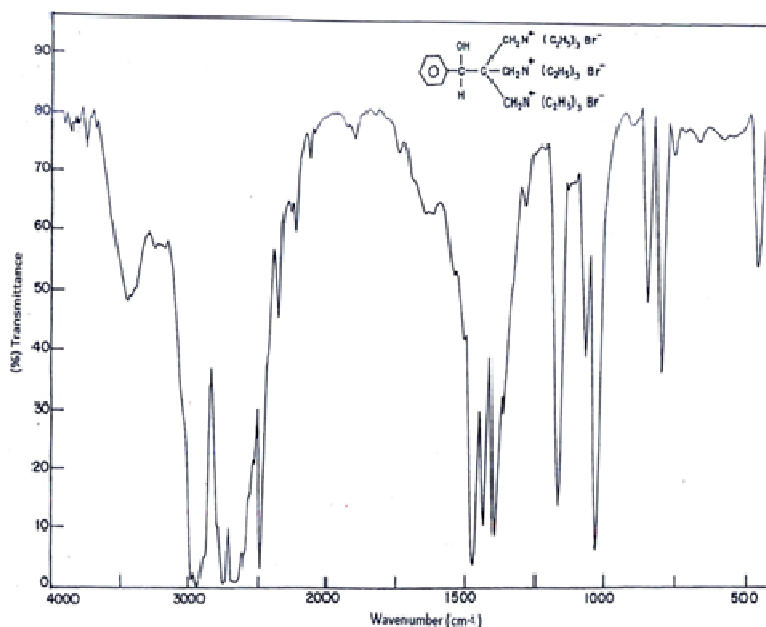


Fig.6 IR spectrum of  $\alpha$ ,  $\alpha^I$ ,  $\alpha^{II}$ -tris (triethyl ammoniummethylene bromide)  $\beta$ -hydroxy ethyl benzene (MPTC-I)

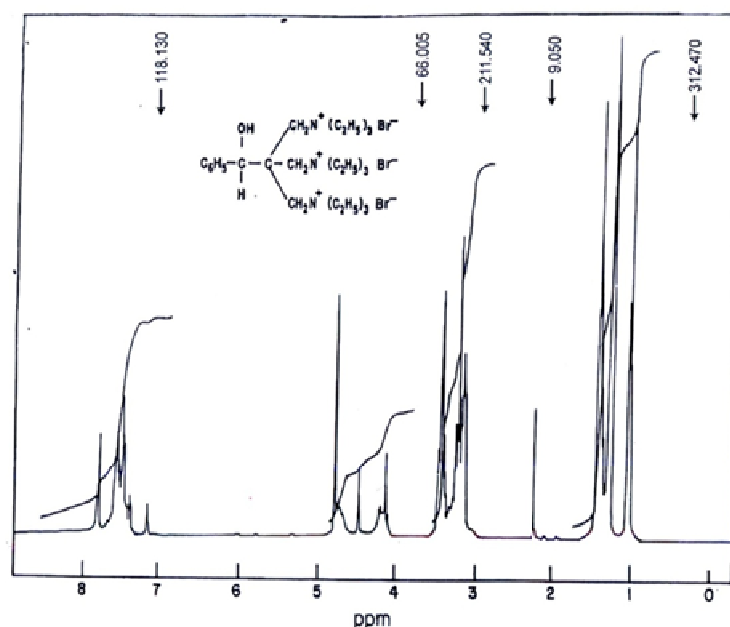


Fig.7  $^1\text{H}$  NMR spectrum of  $\alpha, \alpha', \alpha''$ -tris (triethyl ammoniummethylene bromide)  $\beta$ -hydroxy ethyl benzene (MPTC-I)

### 1.6. Kinetic measurements

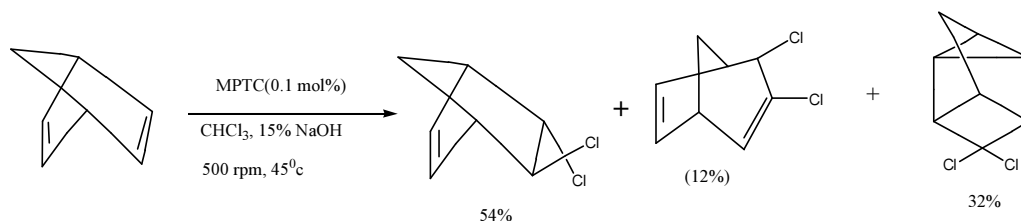
The kinetic measurements were in an ordinary smooth-wall 150cm<sup>3</sup> three-necked flask fitted with flat-bladed stirring paddle, reflux condenser and a pore for adding the components and sampling purposes. All ingredients viz., 25cm<sup>3</sup> of 15% w/w aqueous NaOH (4.41M), 7.04 mg (0.1mol% based on substrate) of the catalyst and 20ml (249.96mmol)  $\text{CHCl}_3$  (solvent) were added. The contents were conditional for about 10 minutes in a thermostat maintained at 45°C before initiating the reaction. Using a mechanical stirrer, the reaction mixture was stirred very slowly. 2 ml of norbornylene preheated to 45°C was added to the reaction mixture. The instant of half delivery of norbornylene was taken as the zero time. The stirring speed was

increased to 500rpm by adjusting the speed with the tachometer. Phase separation was almost immediate after stopping the stirring. The samples were collected from the organic layer at regular intervals of time. A pinch of anhydrous  $\text{CaCl}_2$  was taken in the sample tubes to absorb moisture present in the organic layer if any. Samples were analyzed using Gas chromatograph (Varian 3700 model, vista CDS 401 data system with flame ionization detector) using the column (5% SE-30 Chrom WHP 80/100, 2m 1/8" Stainless tube length). For every run not less than 5 samples were taken and analyzed. Estimating the disappearance of norbornylene followed the reaction. The retention time for chloroform (0.76min), norbornylene (1.00 min) and its product (3,3<sup>1</sup>-dichlorotricyclo [3.2.1.0<sup>2,4</sup>] - octane (1.62 min) were obtained employing auto-

liner temperature programmer (ALTP), 80°C / 2 / 30 / 160°C / 3. The pseudo-first order rate constants were evaluated from the plots of log (a-x) versus time. The reaction was followed up to 80% conversion. A similar procedure was employed for the dichlorocarbene addition to 2,5 – norbornadiene also.

### Graphical Abstract

Three step synthesis of a water-soluble multi-site phase transfer catalyst (MPTC-I), viz.,  $\alpha, \alpha^1, \alpha^{11}$ -tris (triethyl ammonium mehtylene bromide)  $\beta$ -hydroxy ethyl benzene is described. The potentiality of MPTC-I is demonstrated by studying the kinetic aspects of the reactions, viz. dichlorocarbene addition to norbornylene and 2,5 – norbornadiene.



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